JOURNAL OF MATERIALS SCIENCE **32** (1997) 3485–3490

Synthesis and characterization of new precursors to nearly stoichiometric SiC ceramics

Part II *A homopolymer route*

A. TAZI HEMIDA, M. BIROT, J.-P. PILLOT, J. DUNOGUES
Laboratoire de Chimie Organique et Organométallique, URA-35 CNRS-UB1,
Université Bordeaux-I, 33405 Talence, France

R. PAILLER, R. NASLAIN
Laboratoire des Composites Thermostructuraux, UMR-47 CNRS-SEP-UB1,
Domaine Universitaire, Allée de la Boétie, 33600 Pessac, France

---

An original route to SiC ceramics possessing low free carbon($\sim$3.8 at%) and oxygen ($\sim$1 at%) contents is reported. It consists of the polycondensation of 2,4-dichloro-2,4-disilapentane, prepared by Grignard reaction of dichloromethane on methyldichlorosilane. The undesired remaining chlorine was eliminated via a subsequent reduction using lithium aluminum hydride. The synthesis of the ceramic precursor was achieved by thermolysis under argon at atmospheric pressure, with the evolution of hydrogen and methane. The pyrolysis of the precursor provided SiC ceramics in an excellent yield ($\approx$ 79%).

---

1. Introduction

The organosilicon routes to SiC-based ceramics offer several advantages with respect to traditional powder-sintering routes namely: (i) the possibility of obtaining preforms, films, fibres with a small diameter, or matrices via a liquid technique; (ii) an excellent control of the nanostructure, the purity and the chemical composition of the inorganic material; (iii) the elaboration of metastable ceramics not accessible from the common routes.

The commercially available Nicalon [1] and Tyranno [2] fibres prepared by spinning, curing and pyrolysis of polycarbosilanes (PCS) have allowed the development of SiC/SiC composites. However, the presence of oxygen in these fibres induces a decomposition beyond $\approx$ 1100 °C with an evolution of SiO and CO [3, 4], strongly limiting the thermomechanical properties of the fibres. To avoid these drawbacks, the curing of the preceramic fibres is performed using electron beam irradiation (E.B.) instead of oxygen [5]: the so-obtained Hi-Nicalon fibres show improved mechanical properties up to $\approx$ 1400 °C, but are sensitive to oxidation, due to the presence of free carbon in a large concentration (20 at%) [5]. Amongst the approaches which have been recently proposed to improve the mechanical properties of SiC fibres from specific precursors (i.e., different from PCS), one can highlight the dehydropolycondensation of methylsilane [6]. The fibres resulting from this approach exhibit the following properties; an C/Si atomic ratio ≈ 1, O content < 1 at%, a tensile strength of 4100 MPa, and a Young's modulus of 448 GPa. However, methylsilane is a relatively expensive gas. Consequently, attempts to improve the Yajima process are still in progress, and SiC fibres with a composition close to stoichiometric with a maximum tensile strength value of $\sim$ 3000 MPa and a maximum Young's modulus value of 400 GPa have been prepared. After a 10 h heat treatment at 1400 °C in air, the residual tensile strength is $\sim$ 1500 MPa [7, 8].

In this context we have developed two different strategies to obtain SiC-based fibres with a composition close to the stoichiometric value. Firstly the production of polycarbosilanes with an atomic C/Si ratio = 1.5 that produce a C/Si ratio ~ 1 in the final ceramic, since the evolution of methane during the pyrolysis stage decreases this initial ratio and secondly the pyrolysis of a commercially available polycarbosilane under a reducing atmosphere (in the presence of hydrogen). This paper deals with the first approach, the precursor being produced by the sodium polycondensation of 2,4-dichloro-2,4-disilapentane which displays a –Si–CH_2–Si– unit.

2. Experimental procedure

2.1. Solvents and products

The solvents were purchased from the Solvents, Documentation, Synthèses Company (SDS). The toluene was distilled over sodium and then over $LiAlH_4$ before use. The ether was dried on $CaCl_2$ and then distilled over sodium. The pentane and tetrahydrofuran (THF) were distilled over sodium/benzophenone. The dichloromethane was dried through an alumina column. The $AlCl_3$ (Aldrich), $LiAlH_4$ (Aldrich) and $MeSiHCl_2$ (Hüls) were used as received.

2.2. Characterization

Infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, mass spectroscopy, X-ray diffraction (XRD), size exclusion chromatography (SEC), thermogravimetric (TGA) and elemental analyses have been carried out as described in part I [9].

2.3. Pyrolysis

Prepyrolyses were performed in a tubular resistively heated furnace under an argon (grade N56) flow. The samples were placed in an alumina boat and heated at a rate of 1 °C min^{-1} to 1000 °C with a final dwell of 1 h. High temperature pyrolysis was performed in a graphite crucible using a radio frequency coil [10]. The samples were heated at a rate of 30 °C min^{-1} and maintained at a pyrolysis temperature T_p in the range 1100–1600 °C under a high purity argon atmosphere for 1 h. A mass spectrometer (Delsi Nermag Anagaz 200) was connected to the pyrolysis furnace outlet in order to analyse the evolved gases present in the argon flow.

2.4. Apparatus

All the filtrations and manipulations were carried out in a dry glove-box under a nitrogen atmosphere or with an argon line to avoid contamination by oxygen or moisture. All glassware was carefully dried and purged with argon before use. All the used gases were dried through potassium hydroxide columns.

2.5. The preparation of 2,4-dichloro-2,4-disilapentane, 1

The 2,4 dichloro-2,4-disilapentane was synthesized as described in part I [9].

2.6. Preparation of the homopolymer I

In an apparatus similar to that described in [9], toluene (80 ml) and finely divided sodium (8.5 g, 0.37 mol) were successively introduced under an argon atmosphere. Then the 2,4-dichloro-2,4-disilapentane, $\underline{1}$ (28 g, 0.16 mol) was added dropwise over a period of 3 h, to the vigorously stirred and refluxed reaction mixture which was then further refluxed for 48 h whilst under continuous stirring. After cooling, the dark solid was filtered off on a Whatman membrane. Most of the solvent was evaporated by fitting the flask containing the product to a vacuum line, giving crude homopolymer I which was readily reduced.

2.6.1. Characterization of homopolymer I

The ^1H NMR spectrum consisted of broad signals at 0.5 ppm that were assigned to $SiC\underline{H}_2$ and $SiC\underline{H}_3$ a signal at 3.5 ppm that was assigned to $Si–\underline{H}$. Before reduction a weak signal assigned to $MeClSi\underline{H}$ was detected at 4.5 ppm. The experimental $C–\underline{H}/Si–\underline{H}$ integration ratio was found to be 5.5 instead of the theoretical value of 4: (cross-linking involving the partial consumption of Si–H bonds) (Fig. 1). The ^{29}Si NMR (INEPT) spectra showed a signal centred at − 36 ppm (Si–H polarization) $CH_2\underline{Si}(CH_3)HSi$ (Fig. 2) and a signal centred at − 40 ppm (Si–CH_3 polarization) $CH_2\underline{Si}(CH_3)Si_2$ (cross-linking), (Fig. 3). The IR

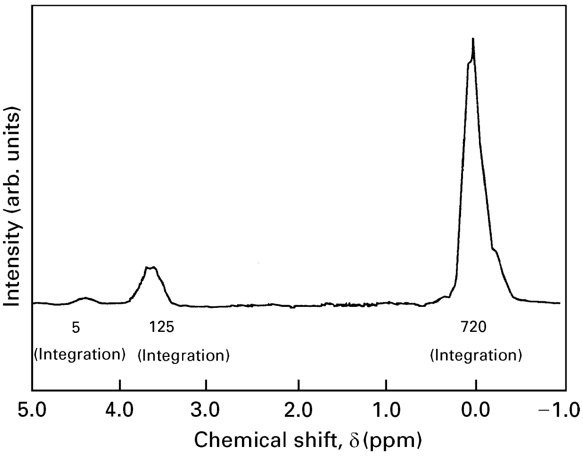


Figure 1 The ^1H NMR spectrum of homopolymer I before reduction.

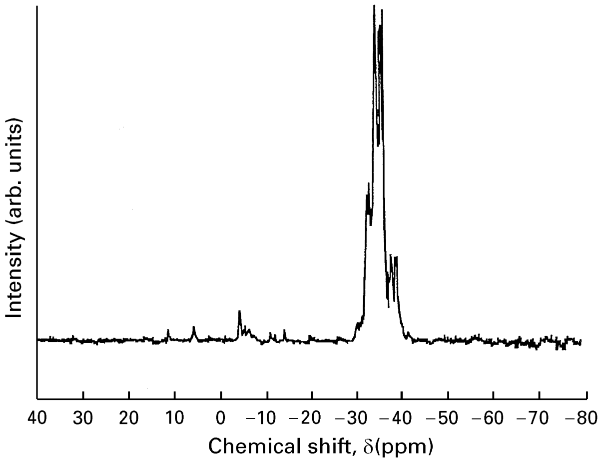


Figure 2 The ^{29}Si NMR spectrum of homopolymer I before reduction (INEPT, Si–H polarization).

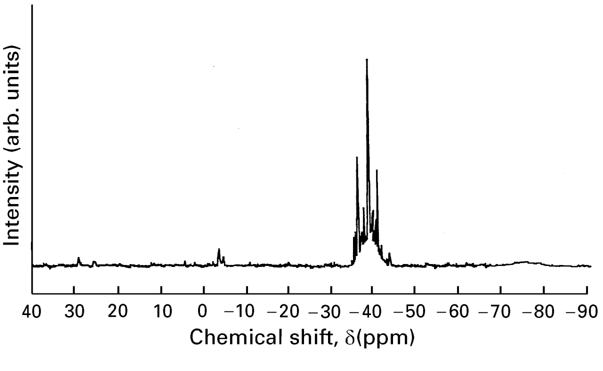


Figure 3 The ^{29}Si NMR spectrum of homopolymer I before reduction (INEPT, Si–CH_3 polarization).

spectrum consisted of absorptions at: (cm^{-1}): 2100 (ν Si–H); 1410 (δ_a CH_3); 1350 (δ CH_2); 1250 (δ_s CH_3); 1040 (W CH_2); 855 (δ Si–H); 687 (ν Si–CH_3). SEC: average molecular weight $\bar{M}_n = 1400$; polydispersuy index $I_p = 3.1$. The ceramic yield was 14%.

2.7. Preparation of the homopolymer II

In the same apparatus as used previously homopolymer I was added, with stirring, to a suspension of $LiAlH_4$ (5 g, 0.13 mol) in ether (150 ml) and then refluxed for 48 h. After cooling, the reaction mixture was slowly poured into aqueous HCl (the medium must be maintained acidic) and washed with water for neutralization. The organic layer was separated and dried over anhydrous $MgSO_4$. After evaporation of the solvent and devolatilization for 1 h at 120 °C, homopolymer II (11.1 g, 67%) was obtained as a yellow liquid.

2.8. Preparation and characterization of the precursors III–V

Silica glassware was used to perform the thermolysis reactions.

Homopolymer II (6 g) was introduced into a 250 ml, three-necked round-bottomed flask inside a dry glovebox. Then the flask was fitted to an argon inlet, a thermometric well, and a reflux condenser connected to a flowmeter via a safety bottle. The vessel was carefully purged with argon, then heated with a fluidized sand-bath to 300–350 °C for 3 h under 1.013×10^5 Pa of dry argon. After cooling under the argon flow, precursor III (3.6 g, 60%) was obtained. This is a yellow solid soluble in most of the usual solvents with a softening temperature of ~ 190 °C (measured by differential scanning calorimetry (DSC)). SEC results: $\bar{M}_n = 2740$, $I_p = 3.3$. TGA residue: 70%.

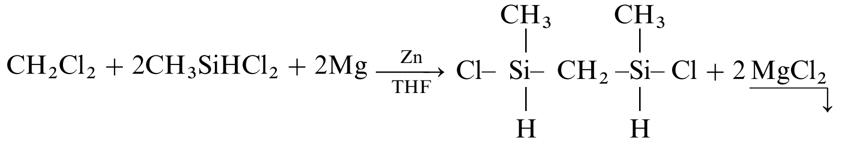
Precursor IV was obtained in a similar manner using the same thermolysis equipment, with the exception that the sample was heated for 7 h (instead of 3 h), due to the absence of a preliminary devolatilization of homopolymer II. The measured IR and NMR spectra of precursor IV are similar to those of precursor III, including the shoulder at 1080 cm^{-1} in the IR spectrum. The yield of the reaction was 60%. The SEC results are $\bar{M}_n = 2550$, $I_p = 3.1$. TGA residue: 60%.

Precursor V was obtained by the thermolysis of homopolymer II for 7 h in an apparatus that had been modified to improve the airtightness. In particular the three-necked flask, the thermometric well, the argon inlet, and the condenser were equipped with silica–metal connections and copper seals. In addition, N56 grade argon was used as the purge gas. Under these conditions, precursor V was obtained also with a 60% yield. The SEC results are $\bar{M}_n = 2570$, $I_p = 3.0$. TGA residue: 79%.

3. Results and discussion

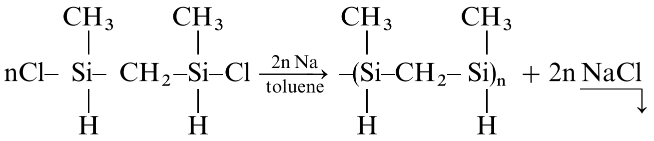
3.1. Synthesis of homopolymers I and II

In order to obtain polymers with a C/Si atomic ratio equal to 1.5, as opposed to the value of 2 for the one prepared by Yajima *et al.* [11], we have performed the homocondensation of 2,4-dichloro-2,4-disilapentane 1, prepared by a Grignard reaction of dichloromethane with methyldichlorosilane [12, 13], in the presence of sodium. Residual chlorine was subsequently reduced with lithium–aluminium hydride yielding polymer II. The reactions were carried out according to the following scheme:



$$CH_2Cl_2 + 2CH_3SiHCl_2 + 2Mg \xrightarrow[THF]{Zn} Cl\text{–}\overset{CH_3}{\underset{H}{Si}}\text{–}CH_2\text{–}\overset{CH_3}{\underset{H}{Si}}\text{–}Cl + 2\,\underline{MgCl_2}\downarrow \qquad (1)$$

I



$$nCl\text{–}\overset{CH_3}{\underset{H}{Si}}\text{–}CH_2\text{–}\overset{CH_3}{\underset{H}{Si}}\text{–}Cl \xrightarrow[toluene]{2n\,Na} \text{–}(\overset{CH_3}{\underset{H}{Si}}\text{–}CH_2\text{–}\overset{CH_3}{\underset{H}{Si}})_n + 2n\,\underline{NaCl}\downarrow \qquad (2)$$

I

$$I \xrightarrow[Et_2O]{Li\,AlH_4} II \text{ (free from chlorine)} \qquad (3)$$

^1H (Fig. 1) and ^{29}Si (Figs. 2 and 3) NMR data showed that polymer I (and presumably II) was somewhat cross-linked by partial consumption of Si–H bonds with an experimental $C\text{–}\underline{H}/Si\text{–}\underline{H}$ ratio of 5.54 (as compared to the theoretical value of 4).

3.2. Preparation of the precursors III–IV

Because of the very low char yield of polymer II (14%), efficient precursors were derived by the thermolysis of II at 300–350 °C under argon, (Equation 4).

$$\text{Homopolymer II} \xrightarrow[Ar,\ (101.3 \times 10^5\ Pa)]{300\text{–}350\ ^\circ C} \text{Precursors III–V} \qquad (4)$$

As detailed in the experimental section, three precursors were prepared. Precursor III was obtained in the primitive thermolysis apparatus from polymer II, after a preliminarily devolatilization at 120 °C under vacuum (5.5 KPa) for 2 h. As the oligomers formed (40% yield) they were also converted into a good precursor at a ~ 70% yield with a subsequent ceramic yield of ~ 60%. Precursor IV was obtained in the same apparatus from the non-devolatilized polymer II, but with a longer thermolysis time. Precursor V was prepared in a similar manner to precursor IV but in the apparatus that had been modified to improve its air-tightness. The TGA and SEC results are summarized in Table I.

The nature and positions of the ^{1}H NMR signals of precursor III are similar to those of the homopolymer I although the signal at 4.5 ppm, assigned to chlorinated end-groups is no longer observed. However, the intensities are different since the $C\text{–}\underline{H}/Si\text{–}\underline{H}$ ratio increased to 6.2. The ^{29}Si NMR spectrum (Fig. 4, Si–H polarization) revealed, in addition to the signal centred at − 40 ppm existing in precursor I, another intense signal at − 13 ppm, which is assigned to $C_3\underline{Si}H$ units, suggesting that the Kumada rearrangement, the insertion of one carbon atom into Si–Si bonds [14] took place to some extent. The IR spectrum of precursor III (Fig. 5) is comparable to that of precursor I however the intensities of the absorption bands were observed to change. A decrease of the band related to Si–H bonds and a small increase of those related to the $Si\text{–}CH_2\text{–}Si$ sequences were noticed. However it must be pointed out that a shoulder at 1080 cm^{-1} (νSi–O(Si)) indicates that oxidation of the sample occurred during the thermolysis step. On the other hand, the IR and NMR data of precursor IV are similar to those of precursor III, including the shoulder at 1080 cm^{-1} in the IR spectrum. For precursor V, this shoulder is not present, revealing a significant drop in the level of oxygen contamination during the thermolysis step.

TABLE I The SEC and TGA data for precursors III–V

Precursor	$\bar{M}_n$	I_p	Char yield at 950 °C (%)
III	2740	3.3	70
IV	2550	3.1	60
V	2570	3	79

3.3. Pyrolysis of the precursors III–V

The pyrolyses of the precursors III–V were performed at 1000 °C and the electron probe microanalysis (EPMA) results are presented in Table II. The free C content is calculated assuming that the oxygen exists as SiO_2 and the SiC is stoichiometric.

With regard to the results obtained with precursor V which should be superior to precursors III and IV, it can be inferred that the homopolymer approach allows a ceramic to be obtained that contains a low level of oxygen contamination and a relatively low percentage of free carbon. The analyses of precursor V pyrolysed at various temperatures are given in Table III.

Due to the low oxygen content, the ceramic composition is relatively stable up to ≈ 1600 °C. The evolution of SiO and CO was not significant.

XRD studies of the materials obtained from precursors IV and V showed that the ceramic is amorphous at 1000 °C but beyond 1100 °C, SiC-β crystallites are progressively formed as the pyrolysis temperature increases. The average crystallite size of the ceramic derived from precursor V is ~ 2.3 nm at 1100°C and 13.9 nm at 1600 °C (Table IV). The ceramics derived from precursors III and IV exhibit a similar behaviour to that observed for precursor V.

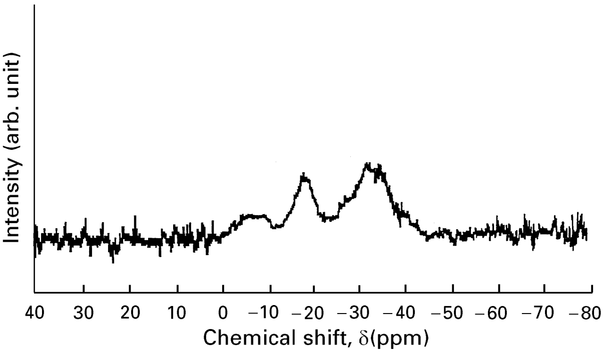


Figure 4 The ^{29}Si NMR spectrum of precursor P III (INEPT, Si–H polarization).

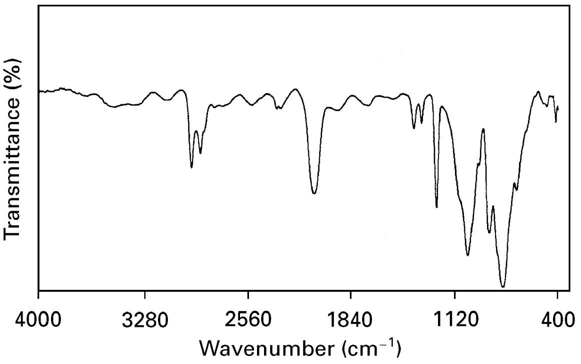


Figure 5 The IR spectrum of precursor P III.

TABLE II EPMA results for the ceramics obtained from precursors III, IV and V

Precursor	Si content (at %)	C total content (at %)	O content (at %)	Free C content (at %)	C/Si (at)
III	42.9	52.6	4.5	12	1.23
IV	47.3	49.8	2.9	4	1.05
V	47.5	51.3	1.2	4.4	1.08

TABLE III EPMA results obtained with precursor V pyrolysed at various temperatures

Temperature (°C)	Si content (at %)	C content (at %)	O content (at %)	Free C content (at %)	C/Si (at)
1000	47.5	51.3	1.2	4.4	1.08
1100	47.6	51.3	1.1	4.3	1.08
1200	47.8	51.0	1.2	3.8	1.07
1600	48.2	51.0	0.8	3.2	1.06

TABLE IV Variation of the crystallite size as a function of the pyrolysis temperature

Pyrolysis temperature (°C)	Average diameter (nm)	
	Precursor IV	Precursor V
1000	1.9	–
1100	2.5	2.3
1200	3.1	2.9
1400	5.8	5.5
1600	14.3	13.9

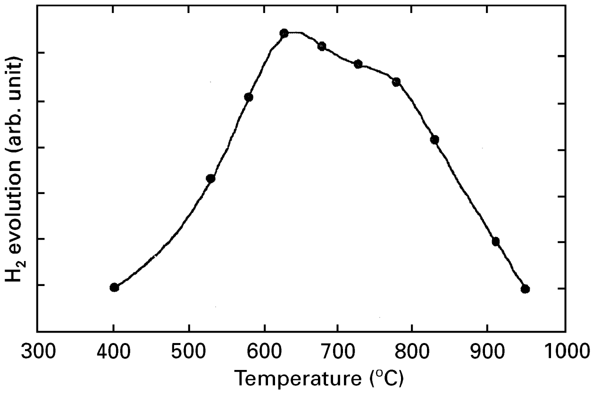


Figure 6 The hydrogen evolution during the pyrolysis of precursor PV.

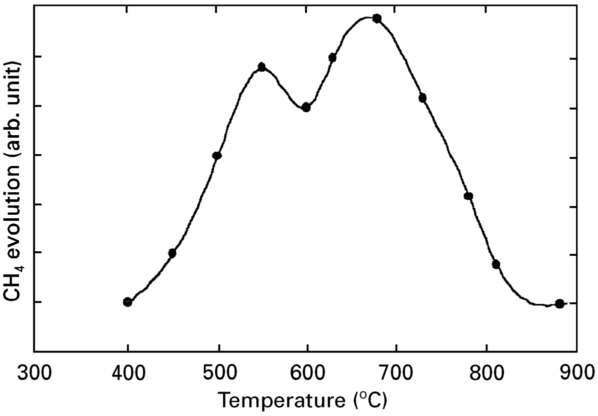


Figure 7 The methane evolution during the pyrolysis of precursor PV.

The main gaseous species formed during the pyrolysis process are hydrogen and methane. The hydrogen is mainly evolved between 400–950 °C with two shoulders at 630 and 730 °C (Fig. 6). The evolution of methane occurs between 400–800 °C with two humps at 550 and 680 °C (Fig. 7). It is thought that, as previously reported for several SiC precursors [15], the evolution of hydrogen is closely linked, at least at the beginning of the pyrolysis, with the disappearance of Si–H bonds, while the formation of methane is related to the methyl groups. The mechanisms for the conversion of the precursor (Yajima-type PCS) into ceramics, including homolytic cleavages have been previously discussed [15] and it has been proved that the SiC network is formed around the silicon atoms as SiC_4 sites, at temperatures lower than those necessary for the formation of CSi_4 nodes.

4. Conclusions

The homocondensation of 2,4-dichloro-2,4-disilapentane constitutes a simple, convenient approach to SiC ceramics with a relatively low free carbon content, without the use of an autoclave. During the heat treatment of the polymers, the formation of carbosilane sequences Si–CH_2–Si, accompanied with the evolution of hydrogen and methane begins at a temperature as low as 350 °C rather than 500 °C as is the case for the commercial polycarbosilane. This result suggests that the transformation of the precursor still occurs in the first stage of the pyrolysis. In addition this approach offers a new entry in the domain of SiC fibres and studies are currently under progress. The homopolymers can be easily thermally branched, at atmospheric pressure and without the use of a catalyst, due to the presence of Si–H bonds. They give soluble, fusible precursors in good yields, which can be spun and converted with a high yield into ceramics. The pyrolysis of these precursors leads to nearly stoichiometric SiC ceramics. In addition, the use of proper synthetic conditions of the precursor allowed us to reduce the atomic oxygen content in the final ceramic to a level as low as 1.2 at%.

References

1. Nicalon from Nippon Carbon Co. Ltd., 2-6-1, Hatbochori, Chu-ko, Tokyo 104, Japan.
2. Tyranno from Ube Industries Ltd., Ube-shi, Yamagushiken 755, Japan.
3. T. MAH, N. L. HECHT, D. E. McCULLUM, J. R. HOENIGMAN, H. M. KIM, A. P. KATZ and H. A. LIPSITT, *J. Mater. Sci.* **19** (1984) 1191.
4. K. OKAMURA, *Composites* **18** (1987) 107.
5. K. OKAMURA, T. MATSUZAWA and M. SATO, *J. Mater. Sci. Lett.* **6** (1987) 826.
6. Z. F. ZHANG, C. S. SCOTTO and R. M. LAINE, *Mater. Res. Soc. Symp. Proc.* **327** (1994) 207.
7. M. TAKEDA, J. SAKAMOTO, Y. IMAI, H. ICHIKAWA and T. ISHIKAWA, *Ceram. Engng. Sci. Proc.* **15** (1994) 133.

8. M. TAKEDA, J. SAKAMOTO, A. SAEKI, Y. IMAI and H. ICHIKAWA, *Ceram. Engng. Sci. Proc.* **16** (1995) 37.
9. A. TAZI-HEMIDA, M. BIROT, J. P. PILLOT, J. DUNOGUES and R. PAILLER, *J. Mater. Sci.* (in press).
10. E. BOUILLON, F. LANGLAIS, R. PAILLER, R. NASLAIN, J. C. SARTHOU, A. DELPUECH, C. LAFFON, P. LAGARDE, F. CRUEGE, P. V. HUONG, M. MONTHIOUX and A. OBERLIN, *ibid.* **26** (1991) 1333.
11. S. YAJIMA, M. OMORI, J. HAYASHI, K. OKAMURA, T. MATSUZAWA and C.-F. LIAW, *Chem. Lett.* **6** (1976) 551.
12. J.-P. PILLOT, C. BIRAN,E. BACQUE, P. LAPOUYADE and J. DUNOGUES, German Patent 3717 265 (French Patent 8607 479 (1986)).
13. *Idem*, *Chem. Abstr.* **108** (1988) 167681.
14. K. SHIINA and M. KUMADA, *J. Org. Chem.* **23** (1958) 139.
15. Y. HASEGAWA and K. OKAMURA, *J. Mater. Sci.* **18** (1983) 3633.

Received 23 February
and accepted 19 December 1996